MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A174 109

REPORT DOCUMENTATION PAGE

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
8		

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
LOW-ELECTRONEGATIVITY OVERLAYERS AND ENHANCED SEMICONDUCTOR OXIDATION: Sm on Si(111) and GaAs(110) SURFACES	Interim; 8/1/84-7/30/86
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
A. Franciosi, S. Chang, P. Philip, A. Wall, A. Raisanen, and N. Troullier	N00014-84-K-0545

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
University of Minnesota 1919 University Ave St. Paul, MN 55104	task NR 372-162

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research Electronics Division (Dr. K. Hathaway) Department of the Navy, Arlington, VA 22217	4/15/86
	13. NUMBER OF PAGES
	19

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; unlimited distribution

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DTIC
ELECTE
NOV 17 1986
B

18. SUPPLEMENTARY NOTES

Submitted for publication to Physical Review B

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Interface reactivity; Catalysis; metal-semiconductor interfaces

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Thin mixed valent overlayers (>1 monolayer) of Sm deposited on Si or GaAs cleavage surfaces prior to oxygen exposure give rise to oxidation promotion effects of unprecedented magnitude. In contrast with this, purely divalent Sm overlayers (thickness <1 monolayer) exhibit negligible oxidation promotion activity. We examine the role of metal electronegativity and metal-semiconductor interface morphology in determining the specific catalytic activity of the overlayer.

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

unclassified

DTIC FILE COPY

LOW-ELECTRONEGATIVITY OVERLAYERS AND

ENHANCED SEMICONDUCTOR OXIDATION:

Sm on Si(111) and GaAs(110) SURFACES

S. Chang, P. Philip, A. Wall,
A. Raisanen, N. Troullier, and A. Franciosi

Department of Chemical Engineering
and Materials Science
University of Minnesota
Minneapolis, Minnesota 55455

ABSTRACT

Thin mixed valence overlayers (≥ 1 monolayer) of Sm deposited on Si or GaAs cleavage surfaces prior to oxygen exposure give rise to oxidation promotion effects of unprecedented magnitude. In contrast with this, purely divalent Sm overlayers (thickness < 1 monolayer) exhibit negligible oxidation promotion activity on Si(111). On GaAs(110) divalent and trivalent Sm species promote the formation of widely different reaction products. We examine the role of metal electronegativity and metal-semiconductor interface morphology in determining the specific catalytic activity of the overlayer.

PACS   79.60Eq   73.40.Ns   82.65.Jv   73.30.+y

86 11 17 070

Control of semiconductor surface reactions through a suitable catalyst could have a dramatic impact in semiconductor technology. Pioneering photoemission work has shown that ultrathin metal overlayers can enhance the oxidation rate of Si(111)[1-4] and GaAs(110)[5-7] surfaces or stabilize new oxide phases on Ge[8]. These studies have mostly focused on noble or near- noble metals, although a few results involve Aℓ[8] and Cs[5] overlayers.

In this letter we report a first photoemission study of the catalytic activity of the low-electronegativity, rare earth metal Sm in promoting Si(111)-O_2 and GaAs(110)-O_2 reactions. We provide evidence of oxidation promotion effects of unprecedented magnitude for Sm overlayers both on Si(111) and GaAs(110) surfaces. A complete analysis of the coverage dependence of this effect and of the stoichiometry of the reaction products is beyond the scope of this paper. Here we focus on the early stages of reaction and investigate the relationship between the valence of the overlayer and its catalytic activity. In particular we report that oxidation promotion on Si is associated only with the presence of intermixed trivalent Sm species. On GaAs, divalent and trivalent Sm species both show catalytic activity, but promote the formation of radically different oxide reaction products.

Samarium was a natural choice for several reasons. First, Sm chemisorption on Si[9], Ge[9] and GaAs[10] seems to follow a two stage process, with a transition between a "weak chemisorption" stage, where Sm is mainly in divalent form and there is little evidence of metal-semiconductor interdiffusion, to a "reactive" stage, where silicide-like interface species are formed, Sm is mostly trivalent, and large core chemical shifts suggest a relevant ionic contribution to Si-metal bonding. The transition between the two stages occurs at approximately 1 monolayer coverage[11], although clustering in the submonolayer region may contri-

bute to some uncertainty in the transition coverage[10]. Because of the coverage-dependent interface morphology, Sm overlayers are an ideal test system to investigate the relationship between morphology and catalytic activity. Secondly, rare earth compounds, and in particular oxides such as Ce_2O_3, have shown catalytic activity in promoting a number of surface reactions of metals[12]. Preliminary work on the $Si(111):Ce-O_2$ system[13] seems to indicate that they may also exhibit relevant catalytic activity for semiconductor surface reactions.

The low-electronegativity of Sm also makes it an interesting system to search for a relationship between metal parameters and overlayer catalytic effects. In the most naive interpretation of catalytic promotion, low-electronegativity elements act as electron "donors" enhancing chemisorption and oxidation processes. Although theoretical studies[14] have demonstrated that the "electron donor" concept is a simplistic description of complex modification of surface/interface states, low-electronegativity overlayers are obviously promising cases in our search for catalysts with maximum specific activity.

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin-Madison following the methodology described in refs. 4, 6-7, and 9. Angular integrated photoelectron energy distribution curves (EDC's) for the Si 2p, Ga 3d and As 3d core emission are shown after subtraction of a smooth secondary background.

In fig. 1 we show representative EDC's for the valence band emission at hv = 60 eV from Sm overlayers on Si(111). The spectra are approximately normalized to the main emission feature and are given in arbitrary units. The bottom-most EDC is for clean Si(111), while the spectra at metal coverages (θ) of 1 and 4 A are representative of two different interface morphologies. In the submonolayer coverage range most Sm atoms are in a divalent "weakly chemisorbed" state so that

Sm^{+2} 4f features visible within 4eV of E_F[10-11] dominate the spectrum. At coverages above a monolayer, trivalent Sm species dominate, giving rise to a characteristic Sm^{+3} multiplet between 4 and 10 eV below E_F. Exposure to 100L of oxygen (topmost EDC $\theta=4$) yields dramatic modification of the valence EDC, which appears dominated by a strong O 2p signal with some residual Sm^{+3} emission. In fig 2. we show the Si 2p core emission before (dashed line) and after (solid line) exposure to 100L of oxygen. The EDC's have been shifted rigidly when necessary to suppress small band bending variations and they have been arbitrarily normalized to the Si 2p feature at the initial "substrate" position to emphasize lineshape changes. The bottom-most EDC shows the effect of oxygen exposure on the Si 2p emission when no overlayer is present. Small oxide-induced features 1-3eV below the main line are consistent with the relatively low oxygen saturation coverage obtainable on the clean Si(111) surface. The vertical bars in fig. 2 at 0.9, 1.8, 2.6 and 3.5 eV mark the position of the chemically shifted Si 2p contributions associated by Hollinger and Himpsel[15] with Si atoms bonded to 1, 2, 3, and 4 oxygen atoms, respectively. Vertical bar α in the top section of fig. 2. marks the position of the dominant Si 2p oxide feature observed by Riedel et al.[16] during oxidation of amorphous silicon.

At submonolayer Sm coverage ($\theta_{Sm}=1$) the unoxidized Si 2p EDC (dashed line) is very similar to the bottom EDC, because of the reduced Si-Sm interaction. Upon oxidation, increased emission is observed on the high binding energy side of the Si 2p cores (solid line), suggesting limited oxide formation and low Si oxidation states. For coverages above one monolayer (top-most EDC), the unoxidized EDC (dashed line) is broadened by the presence of a low binding energy Si 2p component that is the result of the formation of a silicide-like reaction product. Upon oxidation, a dominant Si oxide feature appears where high oxidation states

for Si dominate. The magnitude of the oxidation promotion effect at monolayer coverages and at oxygen exposures of only 10-100L is unprecedented within the series of metal overlayers examined in refs. 2-5. The residual Si 2p emission near the zero of the energy scale appears dominated by a low binding energy oxide feature near 0.75 eV and some residual Si 2p substrate emission, while relatively little is left of the silicide-like emission feature. If higher oxygen exposures are used, the oxide features are further increased relative to the substrate contribution, and no saturation is observed up to 100L exposure. The strong promotion effect phenomenologically corresponds to the presence of trivalent Sm in an intermixed Si-Sm interface region. The oxidation promotion effect observed at submonolayer metal coverage (θ_{Sm}=1) is relatively minor, and could be explained by the presence of a small Sm^{+3} contribution (see fig. 1, θ_{Sm}=1) even at submonolayer coverage, indicating inhomogeneities in the thickness of Sm overlayer[11].

Results for GaAs are shown in figs. 3. The As 3d core emission is shown normalized to the main emission feature after subtraction of the secondary background. The zero of the binding energy scale corresponds to the initial core binding energy for the clean surface in flat-band conditions. The bottom-most EDC is representative of the submonolayer coverage where divalent Sm species dominate. EDC at θ_{Sm}=4 are representative of the coverage range where Sm^{+3} species become dominant. The spectra are shown before (dashed line) and after (solid line) exposure to 1000L of oxygen[18]. If we focus on the unoxidized EDC's, the result of increasing Sm deposition is the emergence of a low binding energy component at about -1.2 eV in the As 3d lineshape, a feature associated with the formation of As-Sm arsenide-like species in the interface region. In the lower section of Fig. 3 we see that at submonolayer coverage, when most Sm atoms are

divalent, oxygen exposure gives rise to a broad emission band between 1 and 4 eV. A minor oxidized feature that emerges near the zero of the energy scale appears related to a small Sm^{+3} contribution visible also in the valence spectra[19]. This contribution also accounts for a shoulder near -1.2eV in the dashed-line spectrum in the lower section of Fig. 3. For θ=4, arsenide-like species involving Sm^{+3} atoms are observed[11] as a major emission feature near -1.2eV, and oxygen exposure gives rise to two well-defined oxidized features: a broad dominant line near the zero of the energy scale, and a high binding energy feature near 3 eV, the latter clearly related to the feature observed at submonolayer Sm coverage. Vertical bars 1-4 in fig. 3 indicate the position of As 3d features observed by Landgren et al.[18] 0.8, 2.3, 3.2 and 4.2 eV below the initial substrate As 3d binding energy, and associated by these authors with the presence of As coordinated with one, two, three and four oxygen atoms, respectively. Vertical bar 5 corresponds to the position of the As 3d core level observed in As_2O_3 by Su et al.[20]. The results of fig. 3 indicate that strong oxidation promotion effects yield the formation of oxidized As species with low-oxidation states and a second phase with higher stability (possibly similar to As_2O_3). The formation of the first oxidized species is related to the presence of Sm^{+3} in the Sm-As interface reaction products, while the second species are related to the catalytic activity of the divalent Sm component. No saturation of oxygen uptake is observed up to exposures of 10^3L.

For the Ga 3d line the discussion is complicated by the superposition with the Sm 5p core features[19]. We anticipate here that upon exposure to 1000L of oxygen little oxidation effect is seen at submonolayer Sm coverage, while at θ=4 most Ga atoms within the experimental sampling depth appear oxidized[19].

In conclusion, we have shown that thin Sm overlayers act as powerful

promoters of the oxidation reaction on both Si(111) and GaAs(110) surfaces. The magnitude of this effect seems to indicate that the naive picture of low-electro-negativity overlayers as "electronic promoters" of chemisorption is somewhat relevant. However, the tabulated metal electronegativity is certainly not the single parameter to be used to forecast promotion effects, since our results indicate, for example, that trivalent Sm atoms strongly bonded with Si at least in part ionically exhibit higher specific activity than divalent Sm overlayers.

Two factors that may play an important role are interface morphology and the formation of intermediate reaction products. In the case of Si, since trivalent Sm species are "dispersed" in an intermixed Si-Sm interface region, they may play the role of a dispersed catalyst occupying "active" surface sites that were not available in the submonolayer, divalent chemisorption stage. Alternatively, the oxidation reaction may take place through intermediate Sm compounds where Sm is in a trivalent state, such as a hypothetical Sm_2O_3 surface oxide. In this connection, we note that the formation of a surface Ce_2O_3 intermediate that acts as a medium for ionic transport is a basic element of a theory recently proposed to explain the activity of Ce overlayers during oxidation of Nb[13]. The occurrence of two different kinds of reaction products on GaAs as a result of the activity of divalent versus trivalent Sm species is unprecedented and could indeed be related to the formation of two different kinds of intermediates (oxides or arsenates) during the oxidation process.

REFERENCES

1. A. Cros, J. Derrien, and F. Salvan, Surf. Sci. 110, 471 (1981); J. Derrien
    and F. Ringeisen, ibid. 124, L35 (1983); A. Cros, J. Phys. (Paris) 44, 707
    (1983).

2. G. Rossi, L. Calliari, I. Abbati, L. Braicovich, I. Lindau, and W. E.
    Spicer, Surf. Sci. Lett. 116, L202 (1982).

3. I. Abbati, G. Rossi, L. Calliari, L. Braicovich, I. Lindau, and W. E.
    Spicer, J. Vac. Sci. Technol. 21, 309 (1982).

4. A. Franciosi, S. Chang, P. Philip, C. Caprile and J. Joyce, J. Vac. Sci.
    Technol. A3, 933 (1985).

5. C. Y. Su, P. W. Chye, P. Pianetta, I. Lindau, and W. E. Spicer, Surf. Sci.
    86, 894 (1979).

6. S. Chang, A. Rizzi, C. Caprile, P. Philip, A. Wall and A. Franciosi, J. Vac.
    Sci. Technol. A. May/June 1986.

7. A. Franciosi, P. Philip, S. Chang, A. Wall, A. Raisanen and N. Troullier, to
    be published.

8. A. D. Katnani, P. Perfetti, T-X. Zhao and G. Margaritondo, Appl. Phys. Lett.
    40, 619 (1982).

9. A. Franciosi, P. Perfetti, A. D. Katnani, J. H. Weaver and G. Margaritondo,
    Phys. Rev. B 29, 5611 (1984).

10. M. Grioni, J. J. Joyce, and J. H. Weaver, Phys. Rev. B32, 962 (1985).

11. Sm coverage is given in Angstroms. In terms of the Si(111) and GaAs(110)
    surface atomic density of 7.8×10^{14} and 8.9×10^{14} atoms/cm^2, respectively,
    it is 1 monolayer = 2.6A on Si(111) and 1 monolayer = 2.8A on GaAs(110).

12. E. E. Latta and M. Ronay, Phys. Rev. Lett. 53, 948 (1984) and references therein.

13. F. U. Hillbrecht, G. Hughes, D. Rieger, F. J. Himpsel, and M. Ronay, Brookhaven National laboratory Internal Report, unpublished.

14. E. Wimmer, C. L. Fu, and A. J. Freeman, Phys. Rev. Lett. 55, 2618 (1985).

15. G. Hollinger and F. J. Himpsel, Phys. Rev. B28, 3651 (1983) and J. Vac. Sci. Technol A1, 640 (1982).

16. R. A. Riedel, M. Turowski, G. Margaritondo and C. Quaresima (unpublished).

17. Results for the free surface (ref. 7) indicate band bending changes with relatively small modification of the As and Ga core lineshape in this exposure range, as expected because of the low oxygen saturation coverage observed in these conditions[18].

18. G. Landgren. R. Ludeke, Y. Jugnet, J. F. Morar, and F. J. Himpsel, J. Vac. Sci. Technol B2, 351 (1984).

19. Detailed coverage-dependent and exposure-dependent results will be reported in a longer forthcoming paper: P. Philip, S. Chang, A. Wall, P. Soukiassian, and A. Franciosi (unpublished).

20. C. Y. Su, P. R. Skeath, I. Lindau, and W. E. Spicer, Surf. Sci. 118, 257 (1982).

FIGURE CAPTIONS

Figure 1. Valence band emission at hv = 60eV for Si(111) surfaces with Sm overlayers representative of the submonolayer (θ_{Sm} = 1A) divalent chemisorption state and of the reactive stage (θ_{Sm} = 4A) where Si-Sm silicide-like species are formed. Sharp emission features between 5 and 0 eV mostly reflect Sm^{+2} 4f final state multiplets (see ref. 10-11). The trivalent Sm 4f final state multiplet appears between 10 and 5eV. The topmost spectrum shows the effect of exposure to 100L of oxygen for the θ_{Sm}=4 overlayer. The final lineshape reflects a dominant O 2p contribution superimposed with residual Sm^{+3} 4f emission.

Figure 2. Si 2p core emission before (dashed line) and after (solid line) exposure to 100L of oxygen. We show results for the free Si surface (bottom) and for two representative Sm coverages. The broad dashed-line spectrum in the topmost section reflects a low binding energy Si 2p contribution from Si-Sm silicide-like interface species. Upon oxidation, strong promotion effects are observed when trivalent Sm species are present in the interface region. The vertical bars mark the position of Si 2p oxide features associated by Hollinger and Himpsel (ref. 15) with Si atoms coordinated with one, two, three and four oxygen atoms. Vertical bar α marks the position of a Si 2p oxide feature identified by Riedel et al. (ref. 16) during oxidation of amorphous silicon.

Figure 3. As 3d core emission at hv = 85eV from GaAs(110) surfaces before (dashed line) and after exposure to 1000L of oxygen. Before oxidation the result of As interaction with mostly trivalent Sm atoms is the emergence of a low binding energy 3d contribution at about -1.2 eV associated with the formation of arsenide-like interface species. The zero of the binding energy scale corresponds to the initial flat band As 3d binding energy for the free surface. In this exposure range oxidation of the free surface

yields only minor modifications of the core lineshape while the presence of Sm overlayers yields oxidation promotion effects. Oxidation gives rise to two distinct oxidized As features, one centered at about 3 eV, and a second one near the zero of the binding energy scale that involves lower oxidation states and dominates when Sm atoms are mostly in a trivalent state. The vertical bars 1-4 mark the position of the oxidized As 3d features observed by Landgren et al. (Ref. 18) for As coordinated with one to four oxygen atoms. The vertical bar 5 marks the position of the As 3d core level in As_2O_3, from Su et al. (ref. 20).

Si + O₂
Si 2p Core

- - - - OL
———— 1OOL

hν = 130eV

$\Theta_{Sm} = 4$

α

$\Theta_{Sm} = 1$

$\Theta_{Sm} = 0$
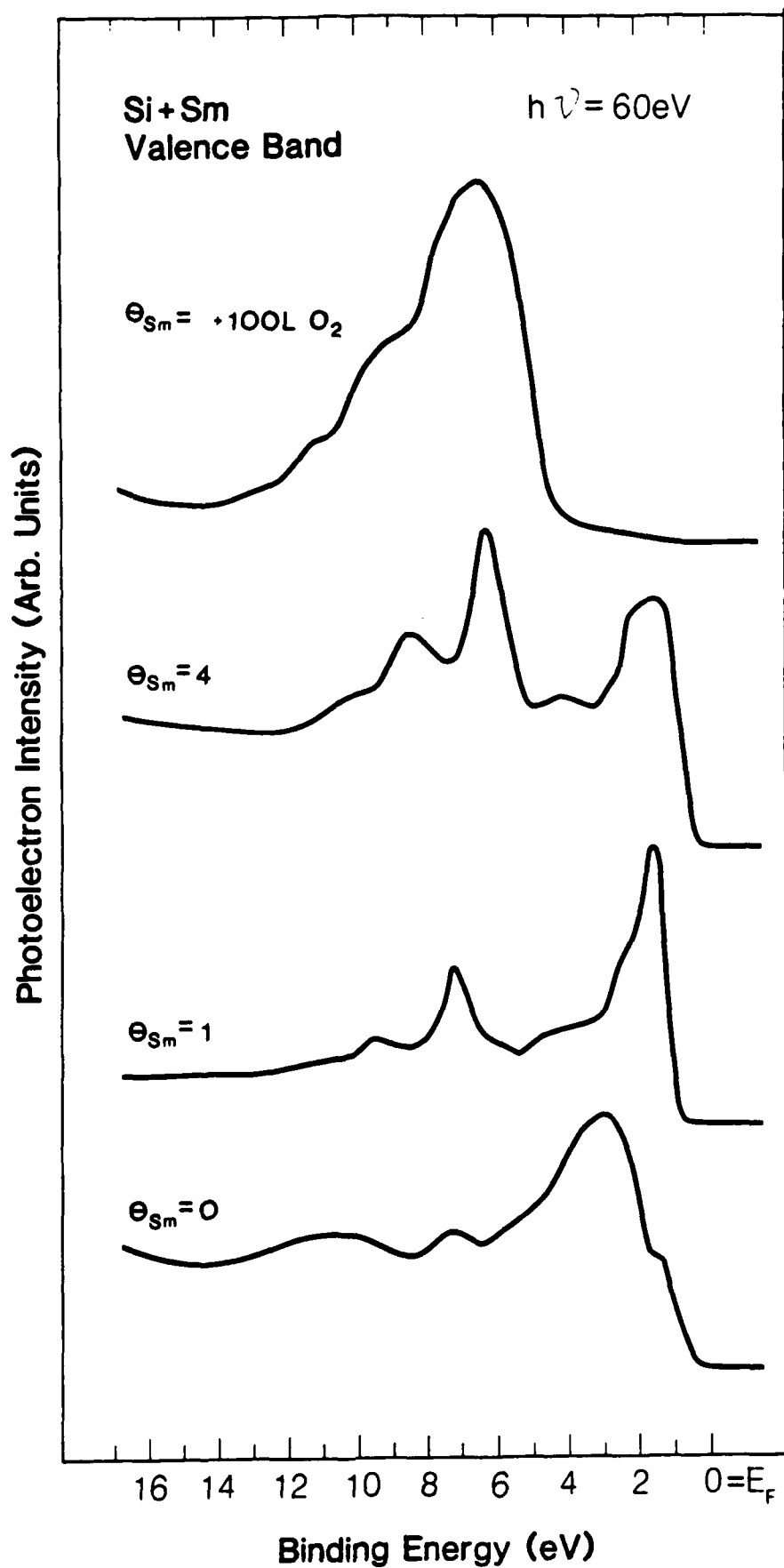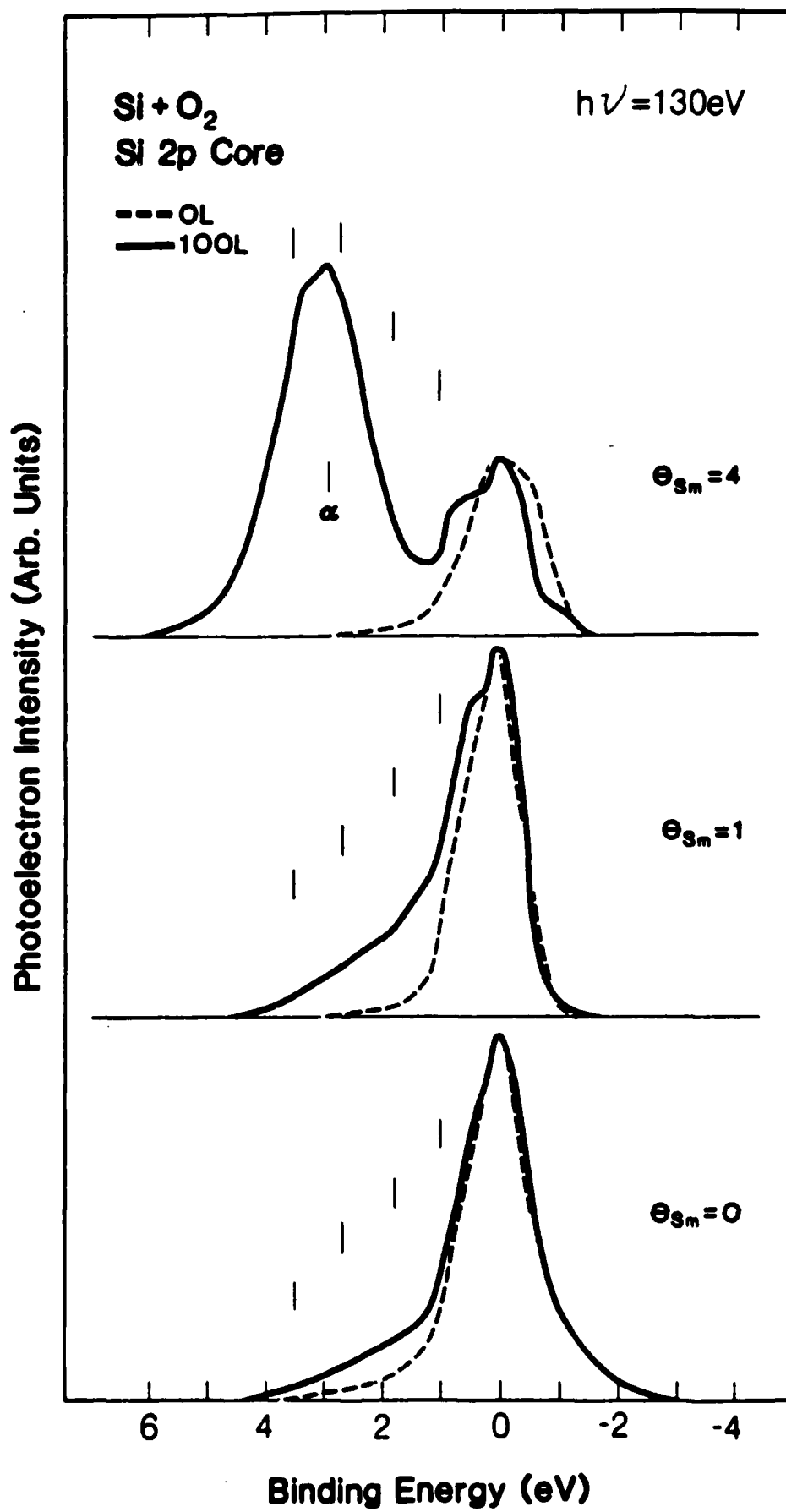
Photoelectron Intensity (Arb. Units)

Binding Energy (eV)

END

12-86

DTIC